

TRANSLATION

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(54) Title:
MAGNETIC RECORDING MEDIUM

(57) Summary

The invention concerns a magnetic recording medium including a nonmagnetic support material and at least one ferromagnetic metal film applied to it as well as a protective layer formed on said metal film from a compound which carries on a partly fluorinated alkyl radical a $\text{H}_2\text{O}_3\text{P-}$, $\text{HO}_3\text{S-}$, $\text{NaO}_3\text{SS-}$, HS or $\text{H}_3\text{C-SO}_3$ radical.

Description

The invention concerns a magnetic recording medium which includes a nonmagnetic support material and at least one ferromagnetic metal film applied to it as well as a protective film formed on said metal film from an organic material.

The magnetic films of a conventional recording supports consist of polymeric organic binders with magnetic oxide or metal particles finely distributed in them. In an attempt to increase the recording density of the magnetic recording support, especially in the field of video and data recording, it was necessary to continually reduce the recording film thicknesses. Such thin films, however, can no longer be achieved with the oxide or metal particle/binder films. Therefore it had already been proposed that thin ferromagnetic metal films be used as the recording films. Chemically or electrolytically deposited ferromagnetic metal or alloy films are already known, especially those of cobalt and/or nickel and above all ferromagnetic films of the metals or alloys such as iron, cobalt, nickel, chromium and rare earths which are vapor coated or sputtered onto the support material.

Such recording supports, however, are usually used in constant mechanical contact with the magnetic head. This means that the surface of the magnetic film must have exceptionally good corrosion and abrasion resistance. However, since the ferromagnetic metal films suitable for the recording films usually do not display the corresponding properties, the formation of protective layers is necessary. In the choice of such protective films it must be kept in mind that neither the application of the protective layer nor the protective layer itself may influence the magnetic film unfavorably in any way.

A large number of proposals for solving this problem have been made. Thus, US-A 3 767 369 describes the application of a rhodium protective film for improving the hardness and the sliding properties, but in this case in order to improve the too low adhesion of the rhodium to the magnetic film a tin-nickel intermediate layer must be applied. This process does not result in

the protective film properties required nor is its application simple and problem-free. For all of those cases in which the metallic magnetic film contains cobalt it has been proposed that this magnetic film be heat treated in air at a preassigned moisture content, thereby oxidizing its surface (US-A 3 353 166, 4 029 541). However, such a process has special disadvantages. Thus the heat treatment process which is necessary for the fabrication of the above-mentioned protective films can influence not only the magnetic properties of the recording film itself but also the commonly used underlying or intermediate layers in such a way that they in turn impair the properties of the magnetic films.

According to other procedures various protective films are applied in a vacuum, usually by sputtering; thus, according to US-A 4 277 540 films of gold, tantalum, niobium, platinum, chromium, tungsten and rhodium as well as the nitrides or carbides of silicon, zirconium, hafnium, and titanium, and according to US-A 4 268 369 films of silicon dioxide. Furthermore in DD-A 109 101 for magnetic memories with a metallic thin film protective films of carbon layers grown in a vacuum have been described. Such carbon protective films, however, are little suited for the purely metallic magnetic films because of the insufficient corrosion protection. The production of a cover film of a carbon and hydrogen-containing plasma-polymerized layer is also known (DE-A 35 45 794).

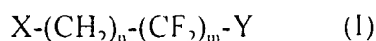
The application of liquid oligomers, e.g., of perfluoropolyethers, to the magnetic film to be protected is also known, e.g., from US patent 3 778 308. Besides the use of different usually fluorine-group-carrying substances such as are described in EP-A 282 188 or EP-A 320 241 for forming protective films the application of combinations of solid and liquid lubricants such as semifluorofluorine [sic] compounds and perfluoropolyethers (DE-A 38 16 467) or carbon films in combination with fluorinated products (JP-A 79 916/1989) as well as carbon films produced by plasma decomposition with organofluorine compounds (US-A 4 816 334) be applied for this

purpose. An important problem in the use of the perfluorinated polyethers is their poor solubility in nonfluorinated organic solvents.

All of these protective layers do indeed bring about an improvement for the problem envisioned, but they are not satisfactory in all properties, above all in abrasion resistance, sliding properties and fatigue strength and with respect to corrosion without at the same time unfavorably influencing the recording properties of the magnetic film.

The problem confronting the invention was therefore to devise a magnetic recording medium with which the protective film generated on the ferromagnetic thin metal film does not have the above noted disadvantages and is also characterized especially by good wear and corrosion resistance.

It has now been found that in the case of a magnetic recording medium including a nonmagnetic support material and at least one ferromagnetic metal film applied to it as well as a protective film formed on the metal film the problem can be solved if the protective film consists of a compound of general formula I



in which

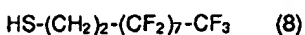
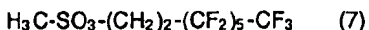
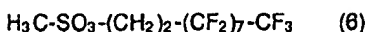
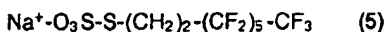
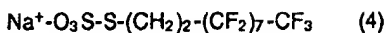
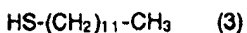
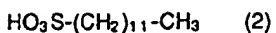
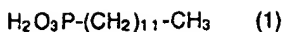
X is a H_2O_3P , HO_3S , NaO_3SS , HS or H_3C-SO_3 radical,

Y is a CH_2 or CF_3 radical,

n is a whole number between 3 and 11, and

m is a whole number between 0 and 7.

Within the scope of the invention substances which are especially suitable for the protective film are the following compounds 1 through 8:



These compounds are produced by conventional methods of organic chemistry. Thus compound (1) is synthesized in two steps by the Arbuzov reaction of dodecyl bromide with triethyl phosphite and subsequent acid hydrolysis of the phosphonic acid diethyl ester. In the case of substances (4) - (8), starting with the fluorinated alcohols by reaction with methane-sulfonic acid chloride compounds (6) and (7) are obtained from which by reaction with sodium thiosulfate compounds (4) and (5) are formed and then by acid hydrolysis of compound (4) the compound (8) is obtained.

The magnetic recording support with a ferromagnetic metal thin film and its construction from nonmagnetic support material, possibly a nonmagnetic intermediate layer and a thin ferromagnetic metal film are well known. As support materials both rigid and flexible materials are commonly used. Disks of aluminum or its alloys as well as disks or foil sheets of polyethylene terephthalate or polyamide are predominantly used.

To form suitable magnetic films the support materials are provided with a nonmagnetic base layer. In the case of plate-shaped aluminum support materials, chemically or autocatalytically deposited amorphous nickel-phosphorus alloy layers with a phosphorus content of 7-11 wt.% are well known. The film thicknesses are ordinarily 5-50, especially 10-30 μm . The nonmagnetic base layers thus applied in the case of aluminum support materials cause an improvement in the workability of the surface compared with the uncoated aluminum supports.

As the ferromagnetic metal thin films the conventional ones with thicknesses of about 300-1500 Å come into consideration which are deposited by known methods by chemical deposition, electrochemical deposition or by vapor coating or sputtering, i.e. deposition of the metals or metal alloys on the support in the high vacuum. Suitable magnetic materials are iron, nickel, cobalt or their alloys with each other or with small contents of other elements. Suitable cobalt-containing ferromagnetic thin metal films include, among others, cobalt-phosphorus, cobalt-boron and cobalt-nickel, cobalt-nickel-iron, cobalt-iron and phosphorus, boron and/or nitrogen-containing alloys of the type mentioned, such as alloys of 95-98% cobalt and 2-10% phosphorus, 30-20% nickel and 70-80% cobalt, 90% cobalt, 9% nickel and 1% phosphorus, 88% cobalt, 9% nickel and 3% boron or 40-50% cobalt, 40-50% nickel and 1-5% boron. With these alloys by chemical deposition on polished substrates films of less than 60 nm thickness can be produced, e.g. with a coercitivity field strength of 20-75 kA/m and a saturation magnetization of 1-1.5 Tesla. Also suitable are ferromagnetic films produced by a sputtering process, deposited possibly on a sputtered-on intermediate layer of chromium. Alloying of chromium into the magnetic film is also known.

The protective film for the production of the recording media according to the invention is produced by the usual method. For this purpose a solution of the compounds of formula (I) is transferred by rolling to the surface of the thin metal film media, and the solvent, which may be tetrahydrofuran, for example, is subsequently removed in a drying channel. The thickness of the protective film on the recording media according to the invention can be adjusted by variation of the parameters of the rolls and the concentration of the substance according to formula (I) in the solvent. A concentration of 0.01-0.04 wt.% has been found to be especially advantageous. At higher concentration the formation of the protective film is nonuniform and problems also arise due to the buildup of the applied substance on the magnetic heads of the recording and

reproducing devices. The application of the compound forming the protective layer can also be accomplished by pulling the recording support through the solution of the substance in question.

The magnetic recording carriers or supports according to the invention display outstanding mechanical strength on the surface as has been proven by the especially high resistance in the case of multiple uses of the recording carrier. Likewise the magnetic recording carrier according to the invention is made very stable by the protective layer against corrosion caused by air or air moisture of the thin magnetic metal films.

The invention will now be explained with reference to the following examples.

For this purpose 0.02 wt.% solutions of the compounds listed in the following table were prepared in tetrahydrofuran. Magnetic tapes consisting of a PET support material and a ($\text{Co}_{80}\text{Ni}_{20}$) film 200 nm thick produced on them by vapor coating were pulled at a speed of about 1.35 mm/s through these solutions. The drying was performed by evaporating the tetrahydrofuran.

Besides the compounds preferred within the scope of the invention, Fomblin-Z-DOL, a perfluoropolyether with terminal hydroxyl groups by the firm Montedison was also used for comparison with the state of the art.

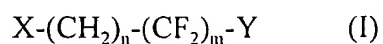
The effect of the protective layer produced in this way on the thin metal magnetic tapes was determined by measuring the superquasistatic friction (SQF). For this purpose the magnetic tapes were pulled in oscillation, i.e. backward/forward over a metal pin. At this time the tension of the tape in front of the metal pin was 30 cN, the looping angle 90° and the test climate 23°C, 50% relative humidity. The measurement of the coefficient of friction was performed at tape speeds of 550 $\mu\text{m/s}$ (V_1) and 13 $\mu\text{m/s}$ (V_2). Small coefficients of friction correspond to low friction between tape and metal pin, in which case above all at the lower feed rate V_2 predominantly adhesive frictional forces are registered.

Table

	Coefficient of friction at	
	V ₁	V ₂
Compound (1)	0.31	0.17
Compound (2)	0.18	0.13
Compound (3)	0.29	0.21
Compound (4)	0.18	0.16
Compound (5)	0.27	0.28
Compound (6)	0.16	0.15
Compound (7)	0.18	0.14
Fomblin-Z-DOL	0.36	0.18

Claims

1. Magnetic recording medium including a nonmagnetic support material and at least one ferromagnetic film applied to it as well as a protective film formed on the metal film characterized by the fact that the protective film consists of a compound of the general formula I



in which

X is a H₂O₃P, HO₃S, NaO₃SS, HS or H₃C-SO₃ radical,

Y is a CH₂ or CF₃ radical,

n is a whole number between 3 and 11, and

m is a whole number between 0 and 7.

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